KINETICS OF PROTON EXCHANGE BETWEEN SEMI-QUINONE RADICALS AND NH-ACIDS

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Using EPR the proton exchange between 3,6-di-tert-butyl-2-oxyphenoxyl, 4-triphenylmethyl-6-tert-butyl-3-chloro-2-hydroxyphenoxyl, and secondary amines was studied. The nature of the solvent had no effect on the kinetic parameters of the process which was attributed to the formation of strong complexes owing to ring type hydrogen bonds. The effect of prototropy on the mechanism of proton exchange was examined.

Keywords: 3,6-di-tert-butyl-2-hydroxyphenoxyl, 4-triphenylmethyl-6-tert-butyl-3-chloro-2-hydroxyphenoxyl, proton exchange, H-acids, EPR, and kinetic parameters.

The present authors have previously shown that the semiquinone radical 3,6-di-tert-butyl-2-hydroxyphenoxyl (1) has the ability to exchange the hydroxyl proton with NH-acids, particularly with primary and secondary aliphatic amines [1]. In an example of the reaction of this radical with diethylamine it was found that the rate of exchange is limited by the proton transfer stage of 1 to the base, which leads to the formation of a contact ion pair of the semiquinone anion-radical with the ammonium cation. The decomposition of the latter is determined by the rate of the change in the spin of the proton of 1 which appears in the EPR spectrum of the radical:

\[ \dot{Q}H + \dot{H}NR_2 \Leftrightarrow \left[ \dot{Q}H \cdots NH R_2 \right] \Leftrightarrow \dot{Q}H^+ + HNR_2. \]  

It was found that in the series of semiquinone radicals, 4,6-di-tert-butyl-3-chloro-2-hydroxyphenoxyl (2), and 4-triphenylmethyl-6-tert-butyl-3-chloro-2-hydroxyphenoxyl (3) there is an increase in both the thermodynamic and kinetic acidity [2]. A consequence of this is that even small additions of diethylamine or triethylamine (c < 10^{-2} mole · liter^{-1}) to toluene solutions of 2 and 3 promote the formation of stable salts of semiquinone anion-radicals with ammonium cations, thereby making these systems inaccessible for the kinetic EPR-analogs [2, 3]. In the present study the characteristics of the kinetics and mechanism of proton exchange of the above-mentioned semiquinone radicals with certain NH-acids, especially with secondary amines with different structures, have been examined. The kinetic parameters of proton exchange between 1 and certain secondary amines obtained in a toluene medium [1] are presented in Table 1. Toluene was selected because of the good solubility of semiquinone radicals in this solvent and because of its relative indifference to reaction partners.

It is apparent from the data in Table 1 that in the series of bases presented, despite the presence of spatial screening of the nitrogen atom and also of other functional groups, which tend to form complexes on account of the hydrogen bond, the specific rates of intermolecular proton exchange have a value of one order of magnitude [k_{exch} (20^\circ C) = 10^8 liter/(mole · sec)]. The activation barrier of reaction (1) correlates with the viscosity activation energy for the solvent toluene (E_v = 8.9 kJ · mole^{-1}) [4]. Furthermore, the spectral measurements showed that additions of weakly secondary basic amines, pyrazole (pK_a = 2.53), diphenylamine (pK_a = 0.5) and others to toluene solutions of 1 did not lead to a noticeable exchange with protons (Fig. 1). In a saturated toluene solution of imidazole (pK_a = 7.03), which is a geometric isomer of pyrazole, an exchange widening of the hfs lines in the EPR spectra of 3,6-di-tert-butyl-2-hydroxyphenoxyl is found with a characteristic decrease in the hydroxyl splitting a, which is associated with the rate of the intermolecular proton exchange reaction [5].
TABLE 1. Kinetic Parameters of Proton Exchange between 3,6-Di-tert-butyl-2-hydroxyphenoxyl and Secondary Amines (solvent — toluene)

<table>
<thead>
<tr>
<th>Secondary amine</th>
<th>(k_{\text{exch}} \times 10^{-8}) (20°C)</th>
<th>(k_{\text{exch}}^{d} \times 10^{-9}) liter/(mole·sec)</th>
<th>(E_a \pm 1.0), kJ/mole</th>
<th>(pK_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylamine</td>
<td>1.7</td>
<td>18.0</td>
<td>10.9</td>
<td>9.93</td>
</tr>
<tr>
<td>Diisopropylamine</td>
<td>4.1</td>
<td>7.6</td>
<td>7.1</td>
<td>9.96</td>
</tr>
<tr>
<td>Dibutylamine</td>
<td>3.6</td>
<td>15.0</td>
<td>9.2</td>
<td>10.83</td>
</tr>
<tr>
<td>Diisobutylamine</td>
<td>4.7</td>
<td>13.0</td>
<td>7.9</td>
<td>10.68</td>
</tr>
<tr>
<td>Diisooctylamine</td>
<td>2.9</td>
<td>15.0</td>
<td>9.6</td>
<td>10.98</td>
</tr>
<tr>
<td>Piperidin 2,2,6,6-Tetramethyl-4-oxypiperidine</td>
<td>2.2</td>
<td>4.0</td>
<td>6.3</td>
<td>11.2</td>
</tr>
<tr>
<td>Morpholine</td>
<td>6.7</td>
<td>21.0</td>
<td>8.4</td>
<td>8.7</td>
</tr>
</tbody>
</table>

\[
v_{\text{exch}} = \frac{\gamma_e a_0}{2 \sqrt{2}} \sqrt{1 - \left(\frac{\tilde{a}}{a_0}\right)^2},
\]

where \(\gamma_e\) is the gyromagnetic ratio for the electron and \(a_0\) is the hfc constant of the unpaired electron with the hydroxylic proton of 1 in the absence of an amine. However, it is difficult to make an accurate determination of the specific rate of proton exchange between 1 and imidazole because of the limited solubility of the latter in toluene.

From the above-mentioned one might conclude that the rate of exchange on the whole is dependent on the basicity of the secondary amine, i.e., the stage of detachment of the proton from 1 by the NH-acid is limiting in reaction (1). In other words, the rapid exchange by protons between 1 and the secondary amines is only possible if protonation of the base precedes this process.

In an attempt to explain this question the effect of the nature of the solvent on the kinetics of reaction (1) was examined. The experimental values of the kinetic parameters of proton exchange between 1 and diethylamine obtained by EPR in different media are presented in Table 2. It was natural to suggest that disintegration of the type C ion pair should exert an inhibitory effect on reaction (1) as occurs in the 1-triethylamine-tributyl phosphate system [6]. However, the data in Table 2 indicate that physical and specific solvation by the molecules in the medium do not have a noticeable effect on the kinetics of proton exchange between the OH- and NH-acids examined.

The observed effect may be attributed to the fact that, owing to the hydrogen bond, the transition complex (the formation of which is essential for proton exchange in the 1-diethylamine system) possesses higher stability than in the analogous complex between 1 and triethylamine, which is decomposed by the reaction of solvating molecules, especially tributyl phosphate. Taking into account the approximate equal basicities of triethylamine and diethylamine one might suggest that the stability of the intermolecular bond of the latter with 1 is caused by the specific structure of the transition complex B formed in which two hydrogen bonds may be present. Taking into account the above-mentioned the general scheme of proton exchange in the 3,6-di-tert-butyl-2-hydroxyphenoxyl—diethylamine—toluene system may be presented as follows:

\[
\text{ROH} + ^{\text{H}}\text{NR}_{2} \rightleftharpoons \text{RO}^{\text{H}} + \text{HNR}_{2} \tag{3}
\]

\[
\begin{align*}
\text{ROH} + ^{\text{H}}\text{NR}_{2} & \rightleftharpoons \text{RO}^{\text{H}} + \text{HNR}_{2} \tag{A1} \\
\text{RO}^{\text{H}} + \text{HNR}_{2} & \rightleftharpoons \text{RO} + ^{\text{H}}\text{NR}_{2} \tag{B1}
\end{align*}
\]

It is apparent that the decomposition of only cyclic complexes, owing to the type B hydrogen bond (CCHB, cyclic complex hydrogen bond), leads to the appearance of the semiquinone radical in which the hydroxyl proton \(\text{A}_1\) has the opposite spin. In

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